

Sub-ppb Oxygen and Moisture Contaminant Detection in Semi-Conductor Processing

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Abstract

This paper describes a technique for measuring trace quantities of oxygen and moisture contaminants present in a semi-conductor and/or containerless processing environment. Monatomic negative oxygen ions, O^- , formed by electron dissociative attachment through interaction with the molecular oxygen and water, are measured to infer the presence of the contaminants. This technique exploits the fact that the cross section for the reaction is greatly enhanced at the resonant energy. The device built to demonstrate this technique combines a small gridded electron ionizer with a conventional mass spectrometer. The concentrations of oxygen have been measured using the method of standard additions by diluting O_2 in N_2 . The lowest detection limit obtained was 1.2 kHz (O^- count rate) at a concentration of 10^{-10} , corresponding to 0.1 ppb. Sensitivity calculations for detecting moisture, and electron and ion trajectory modeling using the SIMION program are presented. The detection of trace quantities of water vapor was attempted, The difficulties with handling water in the experiments is also described.

1. Introduction

Gaseous contaminants such as oxygen, water vapor, nitrogen and hydrocarbons are often present in semiconductor device fabrication [Ref. 1] and containerless materials processing [Ref. 2]. Oxygen and water vapor are some of the most reactive gases and they therefore have the most adverse effects on the operations. These contaminants arise as a result of outgassing from hot surfaces or they may be part of the impurities in the process gas (even in commercial ultra-high purity gases). Sources of moisture are usually from chamber wall and silicon wafer resorption, or as reaction by-product. They can cause surface oxide formation, hence affecting the quality of semiconductor devices; or become unwanted nucleation sites in undercooling experiments.

The measurement and control of residual oxygen and moisture at the sub-ppb level in semiconductor processing is crucial to several production lines, such as the production of highly integrated chips (64-Mb and higher DRAMs, for example). The thin film properties can be irreversibly affected by localized defects caused in the presence of these contaminants. In the case of metal films, the presence of oxygen and/or moisture leads to the formation of an oxide layer, causing a decrease in electrical conductivity, a reduction in optical reflectivity, and corrosion of the metal. Real-time in-situ contaminant monitoring enables the deployment of statistical process control to minimize yield loss.

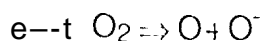
Most commercial instruments for trace oxygen measurement use an electrochemical cell as the sensor element. Solid electrolytic detectors have an oxygen detection limit of around 50 ppb and liquid electrolytic detectors generally have a lower limit. Although the Atmospheric Pressure Ionization Mass Spectrometer (API MS) can potentially measure below one ppb level for many gas species, its complexity, cost, and size limit its utility. A number of vacuum instrumentation has been used for monitoring moisture. Ionization gauges and residual gas (or partial pressure) analyzers are most commonly used. The exposure of these instruments to moisture during operation can sometimes seriously affect their performance. Some sensors determine moisture concentration by measuring the electrical impedance using aluminum oxide. The sensitivities of these sensors are claimed to be in the low-ppb range. However, in some operations, even concentrations below ppb levels have a

detrimental effect on the processing where continuous monitoring is necessary. More sensitive detectors are therefore highly desirable.

This paper describes a technique for measuring trace quantities of oxygen and water vapor at sub-ppb levels that utilizes the resonant electron attachment method. This method exploits the fact that the electron dissociative attachment cross section is largest at the target resonance energy, giving a much higher detection sensitivity and enabling lower concentrations to be measured. It also describes the experimental setup for demonstrating this method. The results for oxygen detection will be presented, along with electron and ion trajectory modeling for water molecules, and the difficulties with handling water vapor in the experiments.

2. Sensitivity Calculation for O⁻ Detection from O₂

When electrons of appropriate energies collide with molecular oxygen, negative oxygen ions, O⁻, are formed. This dissociative electron attachment process can be expressed as:



The detection of O⁻ is used as signature for the presence of the contaminant molecular oxygen. In order to evaluate the capability of this technique and to obtain an estimate of its detection limit, we have performed a calculation based on realistic experimental parameters applicable to our experimental set-up. The detected O⁻ signal count rate, S (in Hz), from electron attachment to O₂ (in single collision conditions) at the resonance energy is given by:

$$S(\text{HZ}) = \kappa \cdot n_T \cdot V \cdot n_e \cdot v_e \cdot \sigma(E) \quad (\text{Eqn. 1})$$

where

E is the electron energy, at the resonant dissociative attachment energy, = 6.8 eV (figure 1).

σ(E) is the cross section for O⁻ production at the resonance energy, = 1.34 × 10⁻¹⁸ cm² [Ref. 3, 4].

v_e is the electron velocity at the resonance energy (6.8 eV), = 15.4 × 10⁷ cm.s⁻¹.

n_e is the electron density, estimated to be $2.6 \times 10^8 \text{ cm}^{-3}$ for a $50 \text{ }\mu\text{A}$ beam.

V is the size of the collision region, which is a spherical volume, estimated to be $- 2 \times 10^{-2} \text{ cm}^3$.

n_T is the molecular oxygen density at room temperature, a quantity to be determined.

κ is the transmission coefficient corresponding to the quadrupole mass efficiency and the loss of ions during extraction, estimated to be -0.005 . This includes the 50% duty cycle.

Assuming a signal rate of 100 Hz is necessary for a reasonable signal-to-noise ratio one may calculate from equation 1 the corresponding value of n_T in the atmosphere to be detected:

$$n_T = 1.86 \times 10^7 \text{ cm}^{-3}$$

This corresponds to a fractional concentration, C , in air of:

$$c = 0.68 \times 10^{-12}$$

where

$$C = n_T / n_A$$

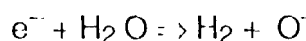
n_A is the molecular oxygen density given above

$$n_A = N_A / V_m = 2.73 \times 10^{19} \text{ cm}^{-3}; \text{ where } N_A \text{ is the Avogadro number } (=6 \times 10^{23}) \text{ and } V_m \text{ is the molar volume at standard temperature and pressure } (=22400 \text{ cm}^3)$$

This calculation shows that this technique is capable, theoretically, of detecting oxygen concentrations in the sub-ppt level.

3. Sensitivity Calculation for O⁻ Detection from H₂O

The dissociative electron attachment process for water vapor can be expressed as:



A similar calculation of the sensitivity for producing O^- in resonant electron attachment with water molecules was also performed. The resonant attachment cross section is a curve with a peak centering around a resonant electron energy of 10.5 eV [Ref. 5]. The maximum cross section value at the peak is approximately $1.48 \times 10^{-18} \text{ cm}^2$ [Ref. 5]. Assuming all the other parameters to be the same as oxygen above and again assuming a signal rate of 100 Hz is necessary for a signal-to-noise ratio of 10 (for an accuracy of 93.30/0), one may calculate, from equation 1, the water density in the atmosphere to be detected:

$$n_T = 1.21 \times 10^7 \text{ cm}^{-3}$$

This corresponds to a fractional concentration, C , in air of:

$$c = 0.45 \times 10^{-12}$$

This calculation shows that this technique is also capable, theoretically, of detecting water vapor concentrations in the sub-ppt level.

4. Experimental Description

An instrument was built to detect the monatomic negative oxygen ions, O^- , as signature for the presence of the contaminants. A schematic diagram of the device is shown in figure 2. Electrons are produced at the filaments F , and are accelerated through a cylindrical grid G . Within G is an electrically-isolated stainless steel tube T which is perforated by several rows of small holes to allow the oxygen molecules to effuse through.

Potentials on F , G and T are arranged so that electrons from F are accelerated towards G , then decelerated and reflected near the surface of the tube. Around this reversal region electrons have a range of energies from near-zero to several eV, depending on the local equipotential. Electron collisions with the oxygen or water vapor effusing through T at the appropriate electron energy (6.8 eV for oxygen and 10.5 for moisture) lead to the process of dissociative electron attachment of the contaminant gas species. The resulting negative ions, O^- , are extracted along the length T by the extraction cone EC and lens L_1 . Ions are focused with a three-element

lens system L_1 , L_2 , and L_3 onto the entrance aperture A of a quadrupole mass analyzer (QMA). They are detected with a channel multiplier (CM), amplified (AMP), and counted by a single-channel scaler with variable counting time.

The electron acceleration and ion extraction are operated in a pulsed mode with 50% duty cycle at a repetition rate of 9 kHz. During the “electrons ON” cycle, typically 12 V potential is applied to **G**. Electrons from F are accelerated through G towards the grounded T and attach to oxygen or water molecules effusing through T. In this phase the voltages on elements EC and L_1 are held at ground so that penetrating fields from these elements do not interfere with fields in the collision region and hence do not distort the motion of the low energy electrons. During the “electrons OFF” and “ions ON” cycle the voltage at G is reduced to -0.05 V and the voltages on EC and L_1 are both raised to approximately 50 V. L_2 and L_3 are set to approximately 170 V and 40 V respectively (not pulsed) to extract the O^+ ions from the collision region.

4.1. Computer Simulation for Water Vapor

Ray tracing simulations were performed using the SIMION program [Ref. 6], for the attachment of water molecules by electrons with energies around 10.5 eV. Figure 3 shows the combined trajectories of electrons and O^+ ions, even though the two processes occur at two different time intervals of the experimental procedure. This curve serves to illustrate the effect of the electric fields on the relative trajectories of the electron and ions during the attachment and ion extraction cycles.

During the attachment period, electrons are accelerated by the cylindrical grid (G biased at 50 V) and then decelerated and reversed at the surface of the tube (T biased slightly negative). Electrons with the resonant energy are available near the surface of the tube. While the electrons are attaching to the water molecules, the extraction cone (C) and the first lens L_1 are grounded in order not to disturb the electrons trajectories. The simulations show that with the present voltage configuration, the electrons are oscillating between the filaments and the tube. This trapping effect allows the electrons more than one opportunity to get attached to a water molecule effusing from the tube, thus enhancing its sensitivity.

During the ion extraction period, the grid and the tube are grounded to prevent interference of the ion extraction cycle by the electrons. The extraction cone as well as

the first electrode of the Einzel lens system are biased positively (100 V). The O^- ions are launched at different positions along the length of the tube with a thermal energy of 0.14 eV at zero angle. This figure also shows O^- ions being extracted as they are formed along the length of the tube and then focused with the Einzel lens system into the entrance aperture of the mass spectrometer. The potentials on the Einzel lenses are $L_1=100$, $L_2=400$, and $L_3=60$ V. Calculation of the equipotentials between the filaments and the tube shows that the equipotential with 10 V is parallel and is at 1.5 mm from the surface of the tube.

5. Results

A mass spectrum corresponding to the negative ions formed in dissociative electron attachment of O_2 is shown in figure 4. The peak clearly visible at $m/e=16$ corresponds to O^- . To determine the analytical capability of this technique, a sensitivity curve was obtained using the method of standard additions [Ref. 7]. Mixtures of O_2 in N_2 (99.99% purity) were prepared at various fractional concentrations C (by particle density) from 1.0 (pure O_2) to 1×10^{-10} , in a stainless steel vacuum system. All lines were thoroughly outgassed to prevent contamination of the mixtures during preparation. The O_2 - N_2 mixture was transferred to the target region which was kept at 2×10^{-7} torr pressure.

The O^- signal was measured as a function of C and the sensitivity obtained from the slope of the standard-additions plot. These results are shown in figure 5. Errors in the data represent the quadrature sum of the statistical counting error, and the error in reading the pressure gauges used to make up each fraction. They are given at the 1.70 (90%) confidence level. The O^- signal S (Hz) has a maximum value $S=21$ kHz in the pure oxygen case ($C=1$) then decreases uniformly to a value of $S=1.2$ kHz at $C = 1 \times 10^{-10}$ (0.1 ppb). Below this concentration, the signal began to fluctuate and a stable reading with the same 90% confidence level was not obtained. Improvements to the stability of the signals in order to increase the measured sensitivity at low concentrations are being pursued. Possible solutions include increasing the electron current (with addition of more filaments) and designing more efficient ion extraction optics.

5.1. Water vapor measurements and experimental difficulties

Figure 6 shows a mass spectrum obtained by introducing moisture in the attachment region. The spectrum corresponds to the negative ions formed in dissociative electron attachment of water molecules and the peak at $m/e=16$ corresponds to O^- ions. However, sensitivity measurements with water vapor were extremely difficult. The method of standard additions described above for oxygen measurements requires stable mixtures over a long period of time. It was not possible to achieve this with the present set-up due to condensations of the water along the transfer lines. This led to large instabilities of the output signal, rendering the data unreliable. Consequently, no sensitivity curve was obtained with water vapor despite intense efforts to maintain a heated line to transfer the water vapor into the vacuum chamber. Alternative methods are currently being explored,

6. Conclusions and Discussion

A technique for measuring trace quantities of oxygen and moisture contaminants present in a semi-conductor and containerless processing environment has been developed. Calculation shows that this technique is capable, theoretically, of detecting oxygen and water vapor concentrations in the sub-ppm level. The device, built to demonstrate this technique, measured a sub-ppb sensitivity level for oxygen. This instrument combines a small gridded electron ionizer with a compact mass spectrometer. The ionizer part itself is no larger than a traditional Bayart-Alpert ion gauge. The ion extraction optics and the mass spectrometer (QMA) represent the bulk of the mass. The maximum operating pressure (10^{-5} torr) is determined by the operation of the QMA. In order for this oxygen/moisture detector to be widely applicable to different industries, for example the semiconductor industry, higher operating pressures (in the milli-torr range) need to be achieved. A miniature assembly of several quadrupoles operating in parallel and mounted on a mini-conflat flange may be a possible solution. This quadrupole array is designed to operate up to 10 mtorr [Ref. 13] which makes it ideal to interface to the ionizer. Furthermore, scaling down the dimensions of the ionizer would decrease the path length of the electrons and ions, thus allowing an increase in the ambient pressure.

7. Acknowledgments

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8. References

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9. Figure Captions

Fig. 1. Cross section for the formation of O^- from O_2 as a function of electron energy. The cross sections are taken from Ref. 4.

Fig. 2. A schematic diagram of the experimental setup to demonstrate the resonant attachment method, where F are the filaments; G, cylindrical grid; T, stainless steel tube through which the oxygen molecules are introduced; EC, ion extraction cone;

L_1 – L_3 , ion extraction lenses; A, entrance apertures; QMA, quadrupole mass analyzer; CM, channel multiplier; and AMP, amplifier.

Fig. 3. Ray tracing simulations using the SIMION program for the attachment of water molecules by electrons with energies around 10.5 eV. It shows the combined trajectories of both electrons and O^- ions (see text for the lens potentials).

Fig. 4. A mass spectrum of dissociative electron attachment of O_2 , showing a peak at $m/e=16$ corresponding to O^- .

Fig. 5. A sensitivity curve for detecting O^- from O_2 , obtained by standard additions for mixing various concentrations of O_2 in N_2 . The solid line represents a least-squares fit to the data. The curve shows a measurement sensitivity down to 1×10^{-10} (0.1 ppb).

Fig. 6. A mass spectrum of dissociative electron attachment of H_2O , showing a peak at $m/e=16$ corresponding to O^- .

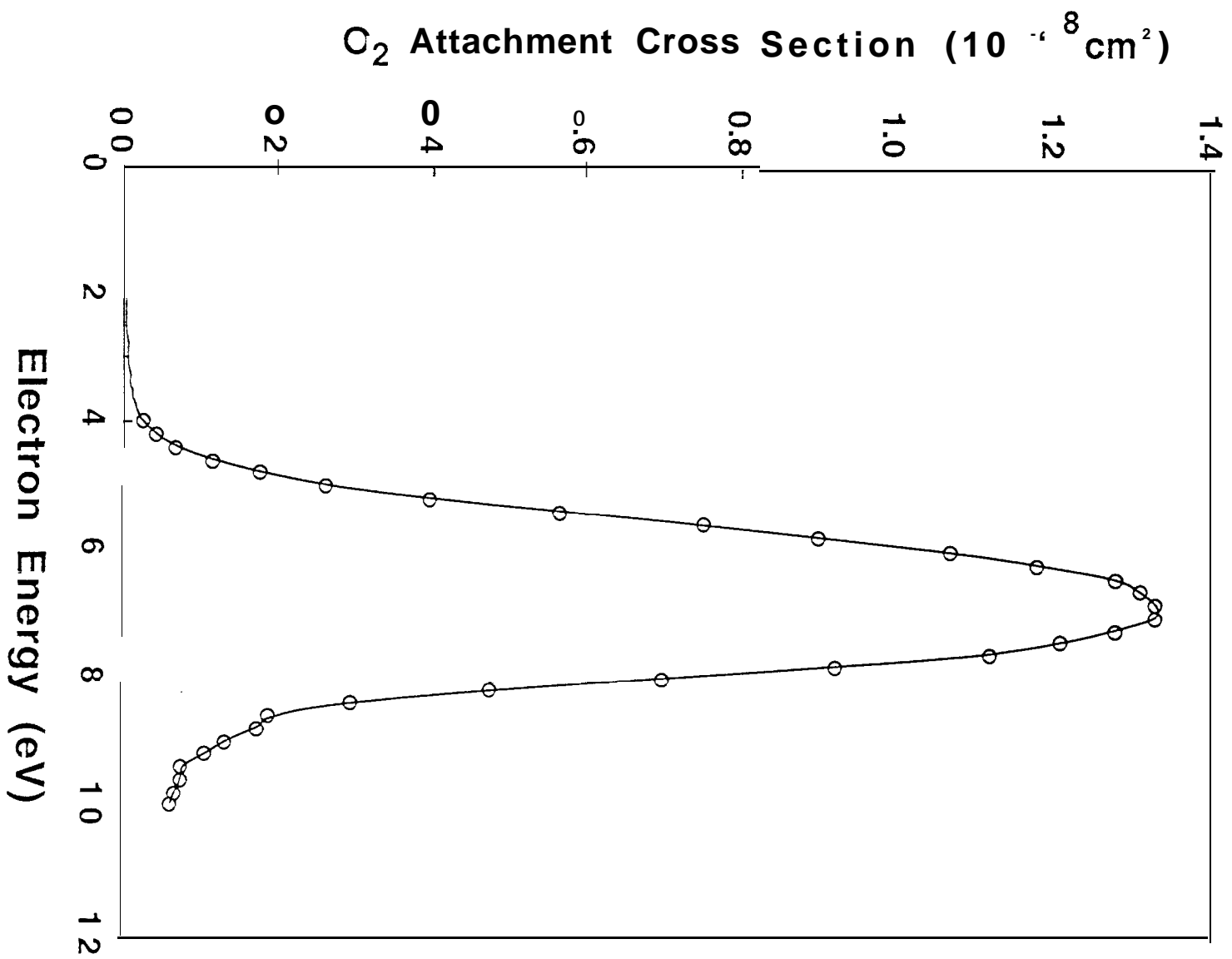
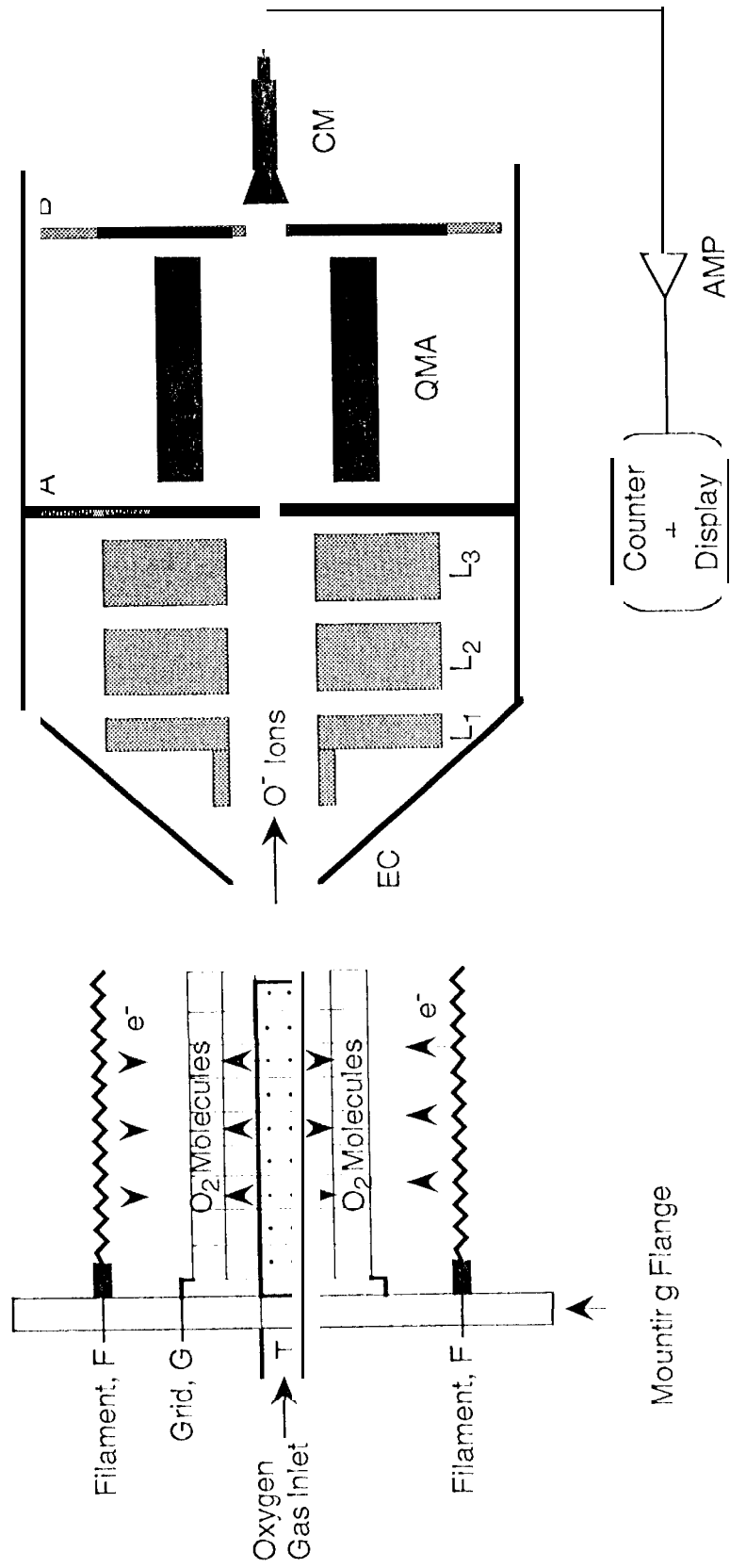
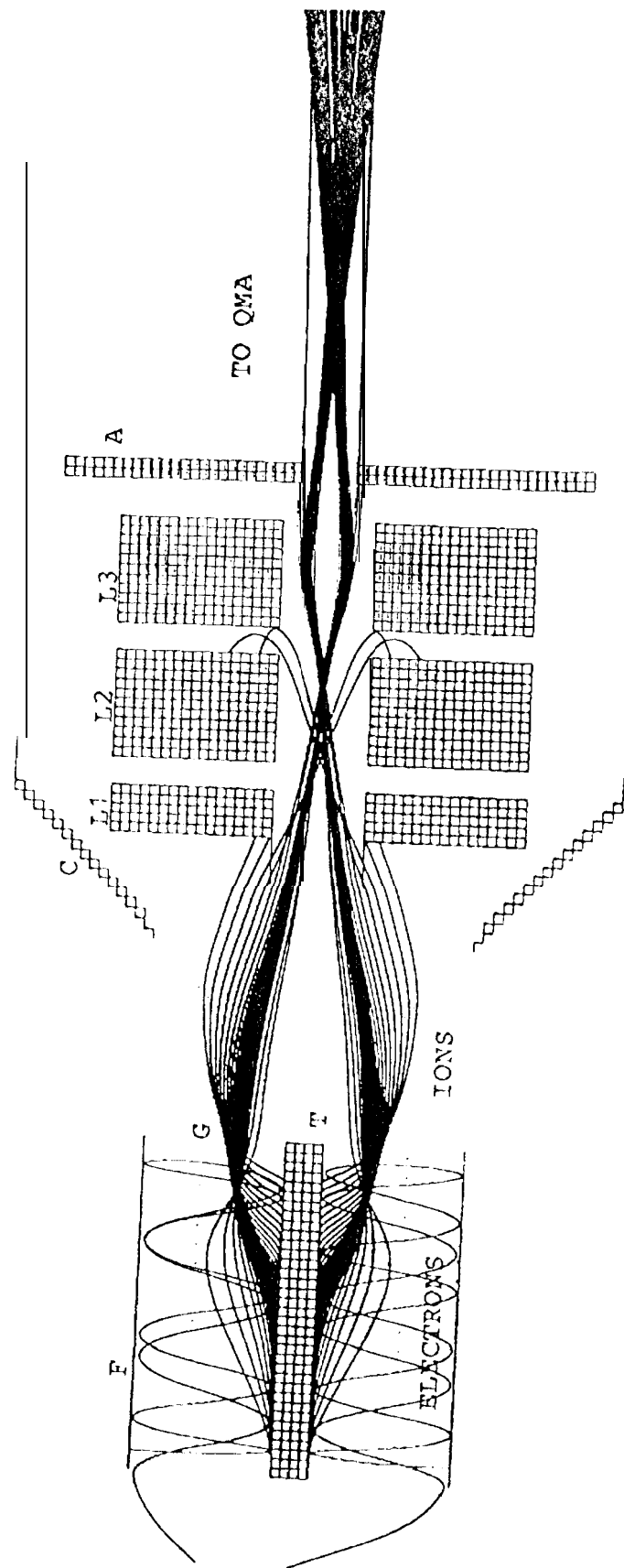


Fig. 1

Fig. 2





SIMION

Fig 3

Fig. 4

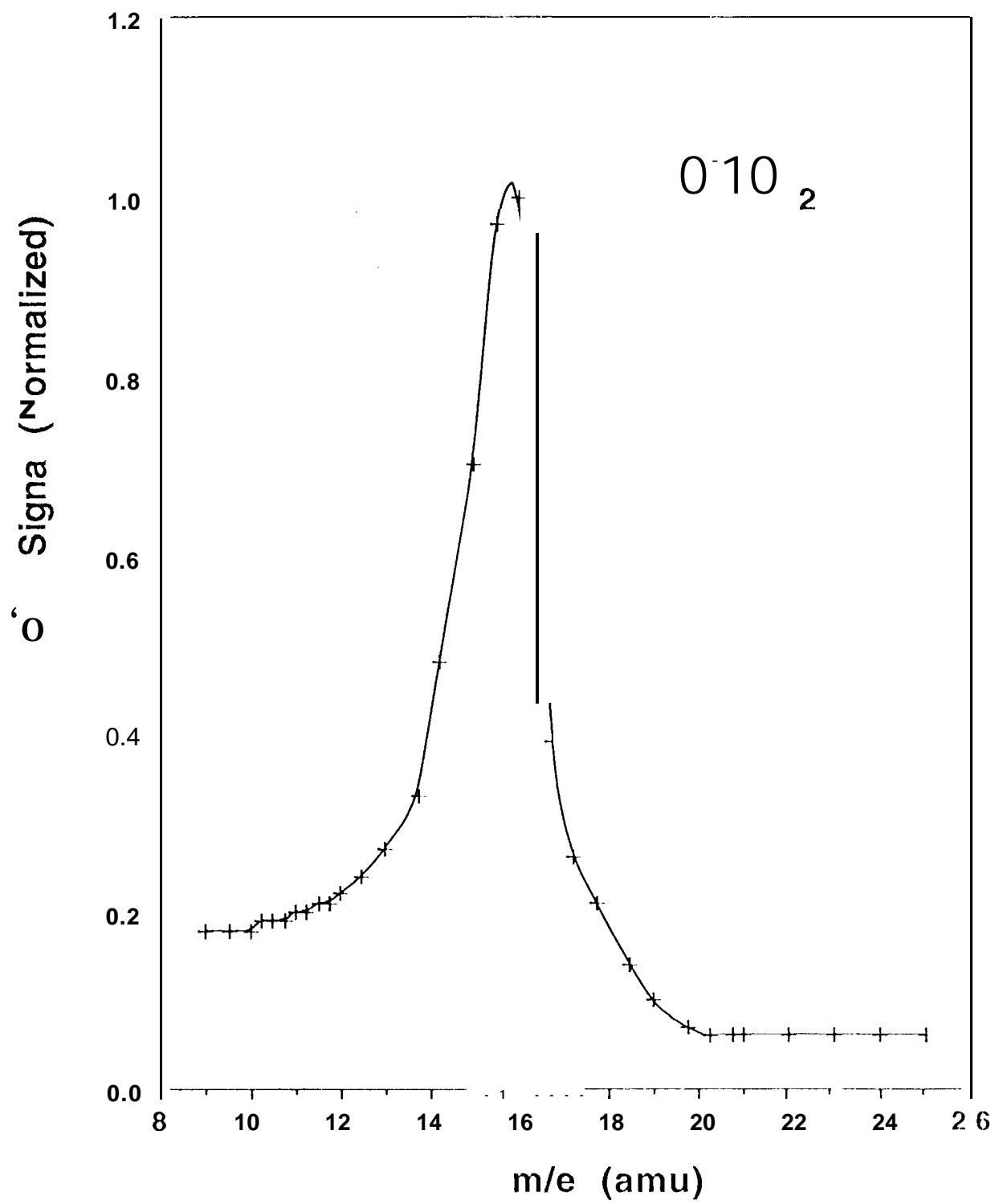
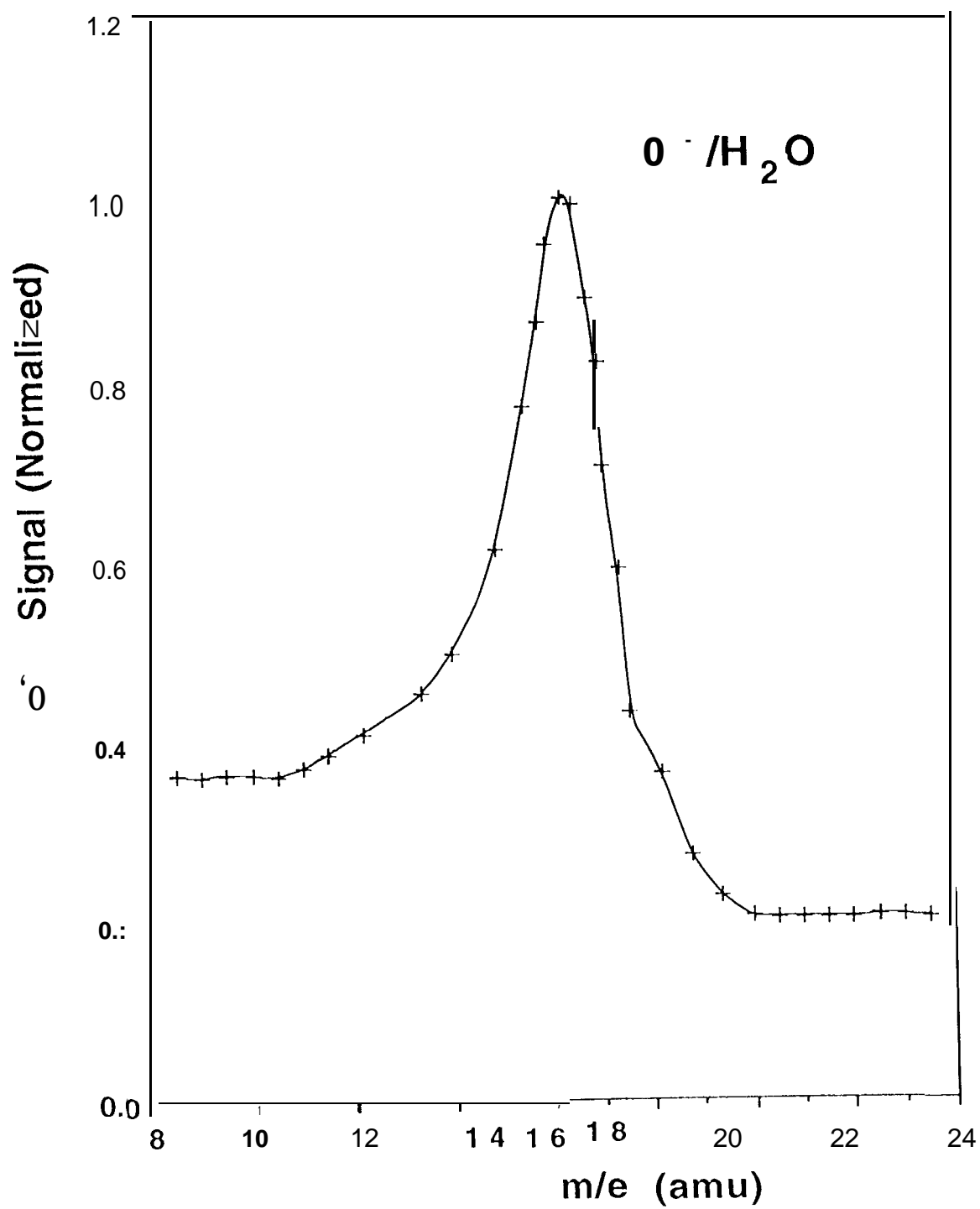


Fig. 5



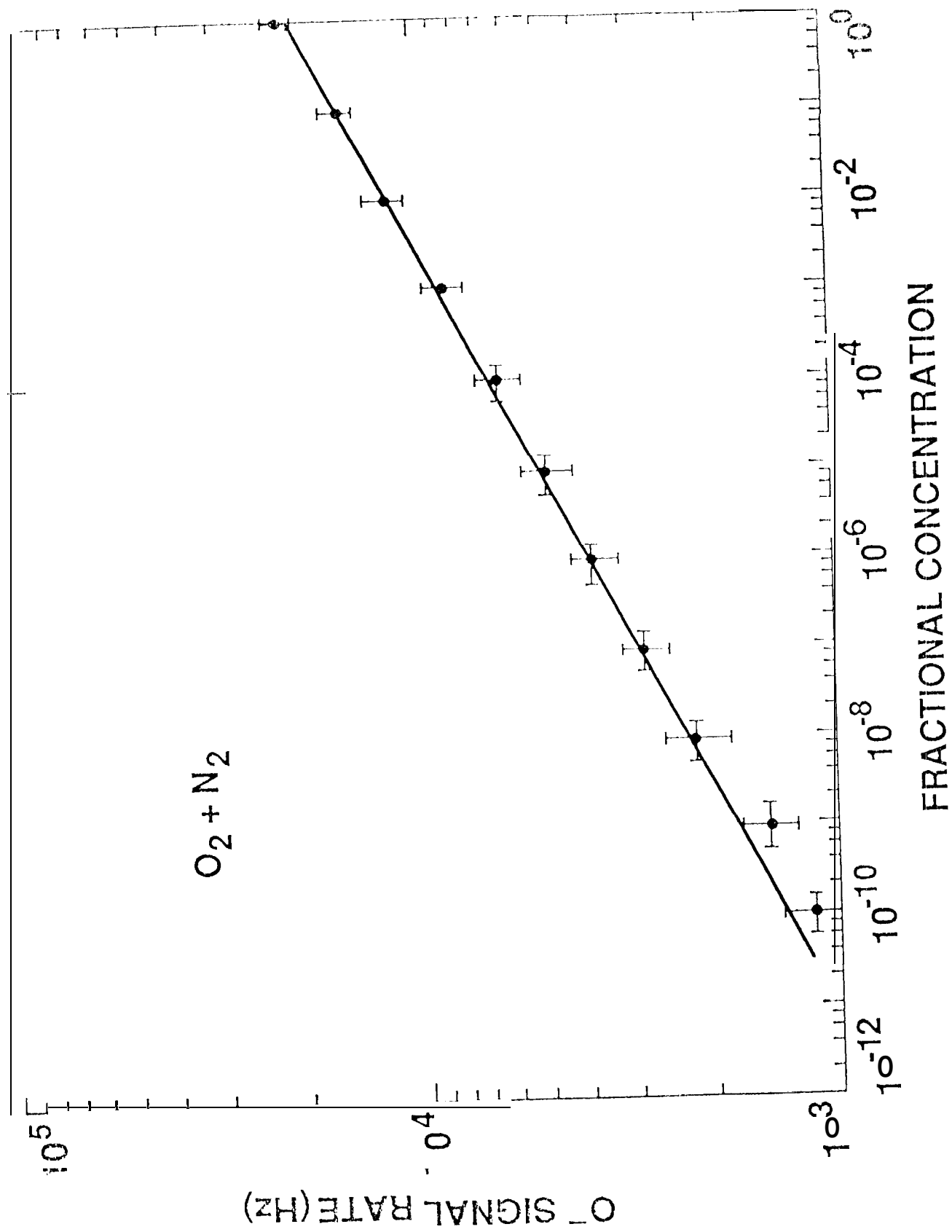


Fig. 6